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(54) Continuous process for polymerizing water-soluble monomers

(57) A continuous process is provided for producing nontacky solid water soluble radical-initiated high molecular weight vinyl polymers. They may be prepared by feeding single phase, high-solids aqueous solution of vinyl monomer(s) at a temperature below the polymerization initiation temperature(s) of such monomer(s) solution concurrently with a solution of water soluble radical polymerization initiator into the inlet of a twin-rotating screw extruder, and venting water from the extruder while maintaining the temperature of the barrels of the extruder in the range of about 80°C to about 100°C to produce the polymer product in a nontacky solid form.

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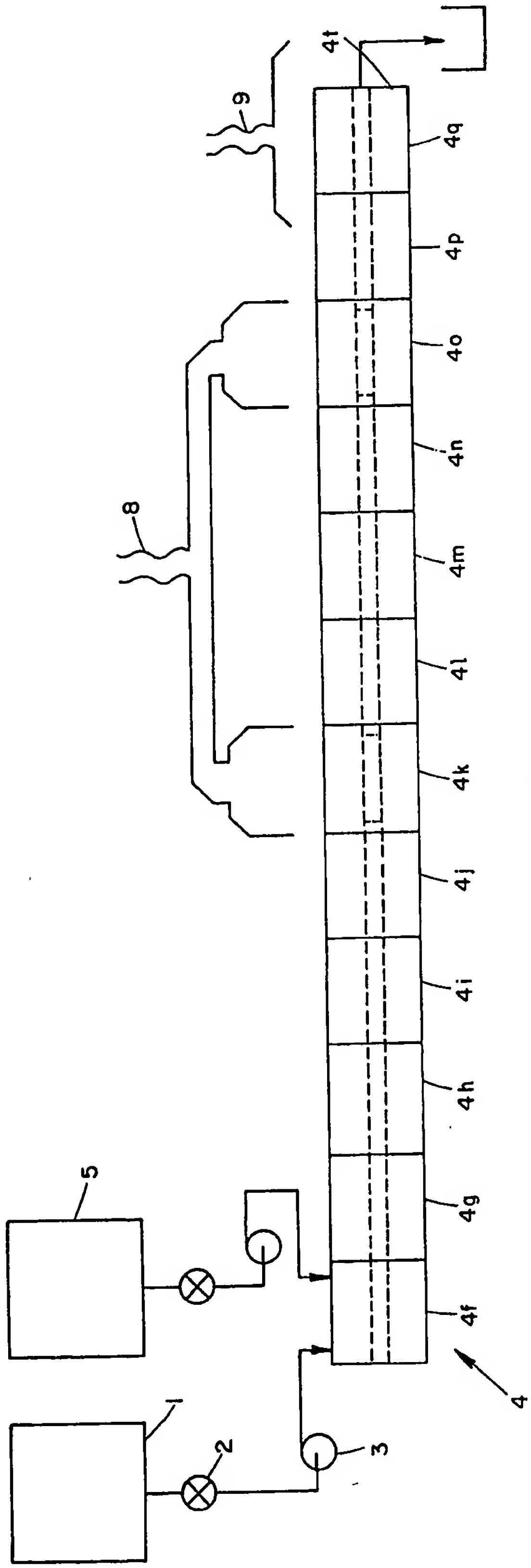

FIG.1

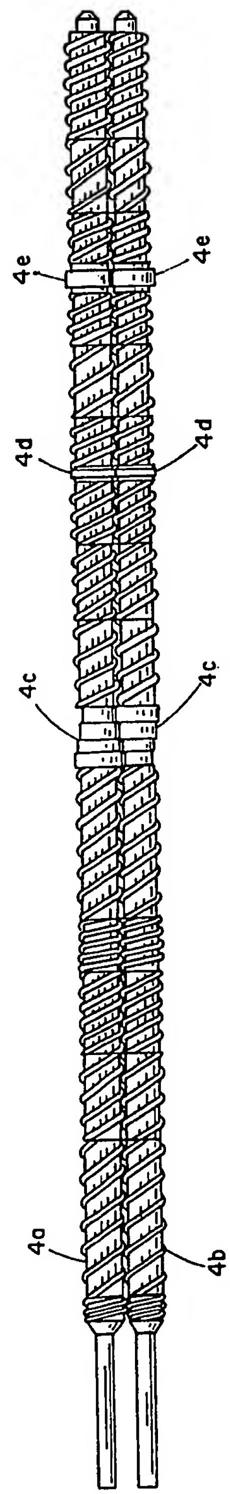

FIG.2

SPECIFICATION

Continuous process for polymerisation of water soluble vinyl polymers

This invention relates to a continuous process utilizing an extruder for producing substantially non-tacky, solid, water soluble, radical-initiated high molecular weight vinyl polymers.

Many processes for producing water soluble polymers have been described. A commonly practised invention has been to homopolymerize acrylamide or copolymerize acrylamide with acrylic acid or an alkali metal salt thereof by a continuous process.

US-A-3,663,518 and US-A-3,732,193 disclose continuous processes wherein preformed solutions of acrylamide monomer mixtures and polymerization initiators are deposited on a moving belt and then heated to initiation temperature, after which they are passed into a polymerization zone. The process of US-A-3,732,193 employs an inert gas atmosphere in the reaction zone.

US-A-4,032,701 discloses a continuous process for producing a dry, solid polyacrylamide, wherein a concentrated aqueous solution of acrylamide monomer is heated to produce a single-phase solution, and this solution is deposited, together with a separately prepared solution of initiator, on a heated rotating metal disc. The heated disc serves to further raise the temperature of the acrylamide/initiator mixture to a suitable initiation temperature, after which an exothermic polymerization reaction occurs to form a dry polymer.

These methods all require heating a mixture of monomers and initiator, after deposition on the moving surface, to reach the polymerization initiation temperature.

According to the methods of US-A-3,663,518 and US-A-3,732,193, the initiator is added to the monomer solution at a relatively low temperature in the monomer tank. The mixture of monomer and initiator is then deposited on a moving surface and heated to the polymerization temperature on the moving surface. This is not entirely satisfactory for the commercial production of the polymers of this invention, because either heat must be applied at such a high rate that very uneven heating occurs, with charring at the heated surface and some thermally initiated polymerization competing with free radical-initiated polymerization, or impractically long distances and/or thin reaction mixture films must be used, which increases equipment and production costs to an economically unacceptable level.

In the process of US-A-4,032,701, the aqueous solution of monomer would be heated in the monomer tank to 50°–100°C. This causes thermally initiated polymerization in the tank, at rates differing from the rates of free radical-initiated polymerization, which results in substantially non-uniform product and causes polymer buildup on the equipment.

Competing thermally initiated and free radical-initiated polymerization is not a problem in the production of acrylamide homopolymer, which is the product made in US-A-4,032,701, but would be a problem with heat sensitive monomer mixtures. This reference teaches heating the monomer solution until a single-phase solution is achieved. In the case of the use of heat sensitive monomers, this temperature is about 30°C, rather than about 50°C, as in US-A-4,032,701. Using the heated disc to raise the temperature of the mixture of monomers and initiator from about 30°C to about 70°C, following the procedure of US-A-4,032,701, would require either inordinately high temperatures for the disc, causing charring and very uneven heating, or an impractically large disc and thin reaction mixture film, again making this alternative economically unacceptable for commercial use.

US-A-4,283,517 discloses a continuous process wherein polymerization of vinyl derivative monomers is accomplished by rapidly heating a single-phase high-solids aqueous solution of monomers to polymerization initiation temperature immediately prior to depositing a uniform layer of the solution and, at the same time, a solution of a polymerization initiator, onto a moving surface. In this patent, the moving surface and the reaction mixture are heated only if necessary to keep the temperature of the reaction mixture from dropping substantially below the polymerization initiation temperature.

Precise control of product composition, homogeneity, and moisture content is not possible using the prior art continuous processes, particularly when a large output rate per minute is desired for economic reasons.

This invention provides a continuous polymerization process for the production of a continuous stream of a solid, non-tacky polymer, comprising the steps of:

(A) forming a concentrated aqueous monomer solution at a temperature sufficient to form a single-phase solution, but insufficient to cause thermally initiated polymerization of the monomer solution; said monomers in the solution being a mixture of at least one water soluble vinyl derivative monomer in water;

(B) continuously applying a stream of said monomer solution to the input end of an extruder having a plurality of multi-barrel co-rotatable conveyor means;

(C) concurrently and continuously applying to the inlet of the extruder a catalytically effective amount of an aqueous solution of a polymerization initiator for the monomers whereby an exothermic reaction occurs to elevate the temperature of the mixed solutions to a level above

the polymerization initiation temperature;

(D) venting one or more spaced barrels to withdraw water vapor resulting from the aqueous solution reaction whereby the resultant polymerized materials have a moisture content of not more than about 18 percent by weight; and

(E) discharging the resultant solid, nontacky substantially dry polymer from the discharge end of the extruder.

Preferably the concentration of the monomer(s) in the aqueous monomer solution is greater than 55% by weight and less than 70% by weight;

Preferably, the aqueous solution of the monomers is formed at a temperature of less than about 40°C.

The present invention is now described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a schematic flow diagram of the process of the invention; and

Figure 2 is a plan view of the conveyor means employed in the extruder.

According to the process of the present invention, a solution of monomers is prepared and held at a temperature high enough to form a single-phase system, but not sufficiently high as to initiate appreciable thermal polymerization in the monomer feed tank, e.g. up to 40°C. At temperatures much above 40°C, thermally initiated polymerization can occur to a substantial degree, and this has undesirable consequences. On the one hand, a skin of polymer tends to form on the surfaces of the mixing tank. Blockages can occur in the feed tube to the extruder utilized in this invention.

The process of the present invention avoids the aforementioned difficulties by forming a homogenous monomer feed solution at a temperature well below that which will cause thermally initiated polymerization and concurrently supplying the monomer feed solution and a polymerization initiation solution to the inlet of an extruder, preferably a dual, co-rotating screw-type extruder. In the extruder, the two solutions are intimately intermixed and an exothermic reaction is created which, with externally applied heat to the extruder chambers, rapidly raises the intermixed solutions to the polymerization initiation temperatures. The temperatures of the intermixed solutions tend to raise rapidly but are maintained at a level around 100°C as the intermixed solutions pass through the extruder. Additionally, at spaced intervals, a venting chamber is provided to conveniently remove water vapor from the partially polymerized solution at these points.

Surprisingly, in less than a minute's residence time in the extruder, the polymerization reaction is completed and the solid polymer is forced out of the discharge end of the extruder as a continuous stream of nontacky polymer solid.

The process of the invention may be used to produce sodium copoly (2-propenamidoalkylsulfonate-2-propenamide) or sodium copoly (2-propenamidoalkylsulfonate-N,N-dialkyl-2-propenamide). Both copolymers may be cross-linked by incorporating any one of a number of divinyl monomers known to those who are skilled in the art. The total percent by weight of the monomers is limited to the water solubilities and mol percent of monomers in the water solution; it is between about 50% to about 70% by weight.

Any (alkali metal salt of) 2-propenamidoalkylsulfonic acid (acrylamidoalkylsulfonic acid) may be used as a starting monomer for preparation of these copolymers, the sodium salt being preferred. Suitable such monomers include, but are not limited to, 2-acrylamidopropylsulfonic acid, 3-acrylamidopropylsulfonic acid, or the sodium salts thereof, preferably, sodium 2-acrylamido-2-methyl propane-sulfonate.

Acrylamide (2-propenamide) and any N,N-dialkyl acrylamide (N,N-dialkyl-2-propenamide) capable of copolymerizing with the sodium 2-acrylamide-2-methylpropane-sulfonate may be used as the comonomer in their respective copolymers.

The preferred N,N-dialkylacrylamide is N,N-dimethylacrylamide.

The mol percent of the monomers in the aqueous solution is not critical in the practice of this invention.

The process of the invention may be used to produce a terpolymer of an alkali metal salt of acrylic acid, a hydroxyalkyl acrylate, and acrylamide.

Any alkali metal salt of acrylic acid may be used as a starting monomer for preparation of this terpolymer, the sodium salt being preferred.

The hydroxalkyl acrylate component of the terpolymer is typically a 2-hydroxyalkyl acrylate or a 3-hydroxyalkyl acrylate, such as 2-hydroxyethyl acrylate, 2-hydroxybutyl acrylate, or preferably, 2-hydroxypropyl acrylate (HPA).

The polymer produced as described above normally has a moisture content of less than about 18%, and usually greater than about 9%, e.g. from about 18% to about 9%. At such moisture levels, the product is nontacky and readily processable into its desired final form.

The product is conveniently ground and milled for example sufficient to pass through a 30-US mesh screen, prior to use. Preferably, the dry product is stored in a moisture-proof container.

The total monomers concentration is normally from about 55 to about 70 weight percent

because it is advantageous to use solutions which are as concentrated as possible, since this facilitates eventual production of a low-moisture content product. Lower concentrations merely increase the heat energy required to produce a nontacky, solid product, slows down the reaction at the lower concentrations e.g. about 55% or lower concentrations, and are not suitable for continuous production.

The pH of the monomers solution is advantageously adjusted to about 5.6–6.7, preferably about 6.2.

The monomer feed for producing the terpolymer is desirably held at a temperature from about 23°C to about 40°C, in the monomer feed tank, preferably about 30°C.

A preferred initiator solution may comprise an aqueous solution of ammonium persulfate with the latter constituting about 2.5% by weight of the solution.

Another preferred initiator solution may be prepared by dissolving from about 2% to 3%, by weight, $K_2S_2O_8$ in water, preferably from 2.70 to 2.85 weight percent. Generally, the volume ratio of monomer feed to initiator feed added to the extruder should be between about 11:1 and about 18:1.

The process of the invention may be more fully understood by means of the following description and in reference to the drawing. As illustrated in Fig. 1, the monomers are normally mixed in a vessel 1 which is advantageously equipped with a conventional stirring means (not shown) and a temperature indicator (not shown). The monomers are fed by means of a valve 2 and a pump 3, to the inlet of an extruder 4.

The initiator solution is separately prepared in a suitable vessel 5 also equipped with a conventional stirring means (not shown). Simultaneously with the supply of monomer solution to the extruder inlet, a suitable quantity of initiator solution is concurrently fed to such inlet. Thus, the two streams are intimately mixed as they enter the extruder 4 and achieve substantial homogeneity shortly after they enter the extruder inlet.

The extruder 4 is a type commonly known as a dual,co-rotating screw extruder, having twin co-rotating screws 4a and 4b (Fig. 2) which are intermeshed so that each screw effects a wiping action on the threads of the other screw. Screws 4a and 4b are provided with kneading sections 4c, 4d, and 4e for further working of the solid polymer. Additionally, extruder 4 is provided with a plurality of axially spaced temperature-controlled chambers 4f through 4q, or 12 chambers in all, to maintain the temperature of the chambers at a desired level, normally about 100%C. This requires supplying of electric heat to the respective chambers, since the exothermic reaction of the monomer solutions generally does not produce sufficient heat to maintain the desired temperature.

At spaced intervals, one or more of the chambers are connected to a vent 8 for withdrawing water vapor emitted from the intermixed polymer solution. End chamber 4q is connected to vent 9 for the same purpose. For this reason, the polymerized mixture issuing from the discharge end 4t of extruder 4 is substantially dry, having only about 12% to 15% moisture content. If further drying or cooling of the product issuing from the extruder 4 is required, such may be accomplished by conventional apparatus well-known in the art.

It will become apparent that various modifications of the general process may be used to achieve substantially the same results. In such modifications are contemplated equivalents of this invention. For example, the cross-linking agent may be applied to the inlet of the extruder 4 as a separate solution concurrently with the comonomer and the initiator solutions. This permits production of either cross-linked or uncross-linked copolymer using the same monomer feed. Alternatively, separate monomer solutions may be prepared and combined in the proper proportions just prior to being fed into the inlet of extruder 4.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. In the following examples, all temperatures are set forth uncorrected in degrees Celsius unless otherwise indicated; all parts and percentates are by weight.

EXAMPLES

Using the aforedescribed apparatus, the mixing vessel 1 was charged with 16.7 kg (24.8 parts) water and 13.6 kg (20.2 parts) 50% weight percent caustic soda. The solution was cooled to about 25°C and 34.9 kg (52.2 parts) 2-acrylamido-2-methylpropanesulfonic acid were added at a rate so that the temperature of the solutions did not exceed 32°C. The final pH of the solution was adjusted to between 8 and 9, followed by addition of 1.9 kg (2.8 parts) N,N-dimethyl acrylamide. The polymerization initiator containing vessel 5 was charged with 0.79 kg of water and 0.01 kg of ammonium persulfate. The monomer and initiator solutions were pumped into Barrel No. 1 of Werner and Pfleiderer ZSK-30 laboratory extruder at the rates of 111.3 l (134.7 kg) per hour at 30°C and 8.7 l (8.7 kg) per hour, respectively, or a volume supply ratuio of about 12.8.

The ZSK-30 laboratory extruder consisted of 12 barrels. Barrel Nos. 5 and 10 were fitted with vents. Barrel Nos. 2 through 5,7 through 9,11 and 12 were heated electrically. Their temperatures were measured by thermocouples placed in Barrel Nos. 2,5,7 and 11. The velocity of screws and pressure of material in the barrels were regulated with the following results:

	Sample 1	*Sample 2*
Barrel 2 temp.	79°C	76°C
Barrel 5 temp.	92°C	97°C
Barrel 7 temp.	83°C	120°C
Barrell 11 temp.	84°C	114°C
Screw Velocity	325 rpm	350 rpm
Material Pressure	483 kPa	276 kPa

	Sample 1	Sample 2
Production Composition, Weight %—		
a) H_2O	40	13.3
b) Polymer	60	86.7
c) Physical State	Tacky, rubber-like.	Solid pea-size pellet.
Viscosity, 2 ppb in deionized water, Fann 35, 300 rpm	34	21
API Filtrate, sea water mud—		
1ppb	21	30
2ppb	14	23

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

Although the invention has been described in terms of specified embodiments which are set forth in detail, it should be understood that this is by illustration only and that the invention is not necessarily limited thereto, since alternative embodiments and operating techniques will become apparent to those skilled in the art in view of the disclosure. Accordingly, modifications are contemplated which can be made without departing from the spirit of the described invention.

CLAIMS

1. A continuous polymerization process for the production of a continuous stream of a solid, non-tacky polymer, comprising the steps of:

(A) forming a concentrated aqueous monomer solution at a temperature sufficient to form a single-phase solution, but insufficient to cause thermally initiated polymerization of the monomer solution; said monomers in the solution being a mixture of at least one water soluble vinyl derivative monomer in water;

(B) continuously applying a stream of said monomer solution to the input end of an extruder having a plurality of multi-barrel co-rotatable conveyor means;

(C) concurrently and continuously applying to the inlet of the extruder a catalytically effective amount of an aqueous solution of a polymerization initiator for the monomers whereby an exothermic reaction occurs to elevate the temperature of the mixed solutions to a level above the polymerization initiation temperature;

(D) venting one or more spaced barrels to withdraw water vapor resulting from the aqueous solution reaction whereby the resultant polymerized materials have a moisture content of not more than about 18 percent by weight; and

(E) discharging the resultant solid, nontacky substantially dry polymer from the discharge end of the extruder

2. The process of claim 1, wherein the concentration of the monomer(s) in the aqueous monomer solution is greater than 55% by weight and less than 70% by weight.

3. The process of claim 1 or claim 2, wherein the concentrated aqueous monomeric solution is formed at a temperature less than about 40°C.

4. The process of any one of claims 1 to 3 and including the steps of heating successive barrels of said extruder to maintain barrel temperatures on the order of about 100°C

5. The process of any one of claims 1 to 4, further comprising the additional step of:

(F) additionally heating the polymerised materials subsequent to either step (F) or step (E).

6. The process of any one of claims 1 to 5 wherein the ratio of the volume supply rate of said monomer solution is about 13 times the volume supply rate of said aqueous solution of polymerization initiator.

7. The process of any one of claims 1 to 6 wherein the residence time of the reactants in the extruder is less than about one minute.

8. The process of any one of claims 1 to 7, wherein the monomeric solution comprises:

(1) a mixture consisting essentially of any alkali metal salt of acrylic acid, a hydroxyalkyl acrylate, and acrylamide; or

(2) a mixture consisting essentially of (a) a (meth)acrylamidoalkylsulfonic acid or alkali metal salt thereof and (b) acrylamide or N,N-dialkyl acrylamide; or

(3) mixture (2), further containing a suitable cross-linking monomer;

9. The process of claim 8 wherein, in solutions (2) or (3), components (a) and (b) are in proportions of from 8 to 90 mole percent and from 10 to 92 mole percent, respectively.

10. The process of claim 8 or claim 9 wherein the aqueous monomer solution is solution (1).

11. The process of claim 10 wherein the monomers are sodium acrylate, 2-hydroxypropyl acrylate and acrylamide, in proportions of 16 to 27 mole percent, 3 to 5 mole percent, and 70 to 80 mole percent, respectively.

12. The process of claim 8 or claim 9 wherein the aqueous monomer solution is solution (2).

13. The process of claim 12 wherein the monomers are 2-acrylamido-2-methylpropanesulfonic acid or the sodium salt thereof, and acrylamide.

14. The process of claim 8 or claim 9 wherein the monomer solution comprises 2-acrylamido-2-methyl-propanesulfonic acid, and N,N-dimethyl acrylamide.

15. The process of claim 8 or claim 9 wherein the aqueous monomer solution is solution (3).

16. The process of claim 15 wherein the monomers are 2-acrylamide-2-methylpropanesulfonic acid or the sodium salt thereof, acrylamide, and a suitable cross-linking agent.

17. The process of any one of claims 1 to 16 wherein the polymerization initiator is ammonium persulfate.

18. The process of any one of claims 1 to 16 wherein the polymerization initiator is potassium persulfate.

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